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## Catalytic depolymerisation of isolated lignins to fine chemicals using a Pt/alumina catalyst: part 1—impact of the lignin structure†

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Four lignin preparations with different contents of alkyl–aryl ether bonds were depolymerised using an alumina supported platinum catalyst. The results showed that the proportion of  $\beta$ -O-4 linkages is the crucial factor for both the yield and the nature of the monomeric products. Highly condensed lignin generated mainly non-alkylated phenolic products while uncondensed lignin generated mainly phenolic products retaining the 3-carbon side-chain. These phenolic products with the 3-carbon chain still attached were considerably less abundant than the maximum potential yield calculated from selective cleavage of alkyl–aryl ether bonds by thioacidolysis, demonstrating that the scope for improved yield remains. Although the catalytic conversion yield rose with an increasing content of labile ether linkages in the lignin structure, optimisation of the catalytic depolymerisation was increasingly required to minimize side reactions. Gel permeation chromatography showed that the products converged towards the same molecular weight distribution regardless of the starting material. The full potential of the highly uncondensed lignin was reached only after the minimisation of condensation reactions during the catalytic conversion.

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### 1. Introduction

It is widely agreed that the economic viability of biofuel production will depend on adding value to the by-products. Amongst these, lignin, for long considered only as an energy resource, attracts the most interest. Several approaches for upgrading lignin have been described in recent reviews.<sup>1,2</sup> Lignin can be converted to high-grade biofuel by pyrolysis and deoxygenation<sup>3–5</sup> or converted to chemicals with a higher added value using heterogeneous catalysis.<sup>2</sup> The attractiveness of lignin lies in its substituted aromatic structure which, after efficient depolymerisation, should lead to substituted aromatic compounds. However, this will heavily rely on a better understanding of the factors influencing the yield and distribution of products.

Of the known approaches for lignin conversion using heterogeneous catalysis, Liquid Phase Reforming (LPR) and hydrodeoxygenation (HDO) have been the most studied. LPR of kraft lignin led to lower value products (guaiacol) in higher yields while HDO produced higher value, more substituted

products (alkylphenolic compounds) in lower yields.<sup>6</sup> Ethyl-substituted<sup>7</sup> and propyl-substituted monomers<sup>8</sup> have been obtained by catalytic hydrogenolysis of grass lignins, but the yield and distribution of products depended strongly on the lignin structure. Recently two lignin preparations with substantial uncondensed (alkyl–aryl ether) percentages were depolymerised using an alumina supported noble metal catalyst. Although no attempt to correlate the conversion yield to the lignin structure was made, the authors suggested that the presence of alkyl–aryl ether bonds was a key factor for the conversion of lignin to monomers.<sup>9</sup> Complete cleavage of the alkyl–aryl ether bonds in a pure, uncondensed lignin model compound was achieved using a carbon supported bimetallic Zn/Pd catalyst in methanol at 150 °C under 300 psi of H<sub>2</sub>.<sup>10</sup>

In hardwood species, native lignins are held together mainly by alkyl–aryl ether bonds (up to 70% in some species).<sup>11</sup> Unfortunately the pretreatment of lignin prior to depolymerisation often leads to significant depletion of this type of bond and generates C–C bonds that are harder to break.<sup>12,13</sup> The resulting condensed lignin is less suitable for conversion to aromatic chemicals. Severe pretreatment conditions (high temperature and acidic medium) are the primary choice for second generation biofuel production but are well known to increase lignin condensation.<sup>14</sup> The impact of the pretreatment on the catalytic conversion of the lignin to products with an added value has been reviewed.<sup>2</sup> Nevertheless the structure of the lignin immediately before the catalytic

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conversion step is rarely taken into account. To the best of our knowledge, no attempt has been made to investigate the impact of the lignin structure on the yield and distribution of catalytically depolymerised products.

In this study four lignins with different degrees of condensation have been subjected to catalytic depolymerisation using an alumina supported platinum catalyst. The lignins were prepared by pretreatments with potential for the production of biofuels and co-products. The purpose of this study was to evaluate the impact of the lignin structure on its suitability for conversion to fine chemicals. The catalytic conversion was performed using a commercial benchmark catalyst, Pt/alumina. The main objective was to understand the yield and distribution of alkylphenolic products in relation to the initial degree of condensation of the lignin.

## 2. Results

### 2.1. Characterisation of the lignin preparations

**2.1.1. Sugar content and elemental analysis.** The presence of sugars in the isolated lignin can be critical for the catalytic reaction. The sugar compositions of the different lignins are shown in Table 1. The ammonia percolation procedure yielded a lignin-carbohydrate extract from poplar that still contained 20% xylan. Its xylan content was reduced to less than 1% by a mild organosolv post-treatment.<sup>15</sup> The poplar organosolv lignin had a low sugar content and no further purification step was needed. The commercial soda lignin from wheat straw had a higher sugar content but not high enough to make it unsuitable for catalytic conversion.

The elemental compositions are typical of lignins previously reported.<sup>16</sup> The higher nitrogen content of both lignins from ammonia-based pretreatments (AFEX wheat straw and Ammonium Poplar) can be explained by incorporation of nitrogen from ammonia during the pretreatment step.

**2.1.2. Lignin uncondensed fractions.** The uncondensed fractions (*i.e.* percentage  $\beta$ -O-4 bonds) were estimated from the total monomer yield generated by thioacidolysis of the lignins and are reported in Table 2. The linkage percentages ( $\beta$ -O-4,  $\beta$ - $\beta$ ,  $\beta$ -5) were also calculated by NMR cross-peaks in the aliphatic region<sup>17</sup> (Fig. 1) and quantified using the G<sub>2</sub> and S<sub>2,6</sub> cross-peaks in the aromatic region as the reference.<sup>18</sup> The 2D NMR experiments measured the total quantity of  $\beta$ -O-4 bonds, whereas thioacidolysis only took into account monomers

**Table 1** Sugar content and elemental analysis of the different lignins [standard deviation in brackets]

	Sugar content (g per 100 g of lignin)	Elemental analysis (mass %)			
		C	H	N	O
AFEX wheat straw	1.1 (0.1)	59.5	6.4	2.1	31.9
Soda wheat straw	2.6 (0.1)	61.3	5.6	0.9	32.2
Organosolv poplar	0.4 (0.1)	63.9	6.0	0.4	29.7
Ammonia poplar	0.5 (0.1)	60.2	6.0	1.8	31.9

**Table 2** Lignin  $\beta$ -linkage percentages and monomer ratios obtained by thioacidolysis and 2D NMR [S: syringyl; G: guaiacyl; H: *p*-hydroxycinnamyl units – standard deviation in brackets]

	Thioacidolysis		HSQC-NMR			
	$\beta$ -O-4	S/G/H ratio	$\beta$ -O-4	$\beta$ - $\beta$	$\beta$ -5	S/G/H ratio
Soda wheat straw	2.8 (0.3)	0.51/0.49/0	3.7	1.9	0.4	0.46/0.40/0.13
AFEX wheat straw	16.8 (0.4)	0.49/0.46/0.06	37.1	4.3	3.4	0.36/0.60/0.04
Organosolv poplar	9.2 (0.2)	0.57/0.43/0	12.2	5.0	4.4	0.48/0.52/0
Ammonia poplar	28.9 (0.3)	0.65/0.35/0	44.9	2.3	9.0	0.64/0.36/0

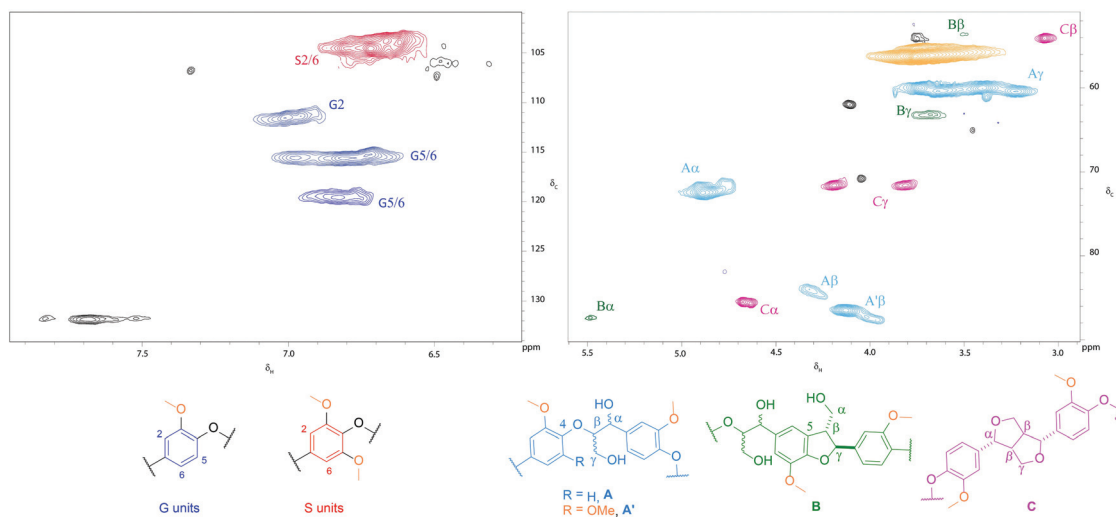
linked by two  $\beta$ -O-4 bonds (the uncondensed fraction). Despite the difference in what was measured, both techniques gave values of the same order for the uncondensed fractions in the four lignins.

As shown in Table 2, the Poplar ammonia lignin showed the highest content of  $\beta$ -O-4 bonds (44.9%), compared with only 3.7% in the wheat straw soda lignin. The difference in the uncondensed fraction comes partly from the feedstock type but principally from the pretreatment conditions. It may be assumed that harsh alkaline conditions were responsible for the condensation of the wheat straw lignin. In comparison the lignin obtained by mild alkaline organosolv extraction of AFEX-pretreated wheat straw retained 37% of  $\beta$ -O-4 bonds, which can be explained by the relative lack of condensation during both the AFEX pretreatment<sup>19</sup> and the subsequent lignin extraction step. After organosolv pretreatment of poplar, the proportion of  $\beta$ -O-4 linkages was reduced to 12%. This is expected since the acidic conditions combined with high temperature (180 °C) are known to cleave  $\beta$ -O-4 linkages leading to more condensed lignins.<sup>20</sup> Similar temperatures were applied during the poplar percolation pretreatment but we have shown that the use of ammonium hydroxide, a weaker base than sodium hydroxide, limits lignin condensation.<sup>15</sup>

Monomer ratios were also obtained from the aromatic proton S<sub>2,6</sub> and G<sub>2</sub> of the 2D NMR (Fig. 1 and S1†). The 2D NMR experiment measured the total amount of guaiacyl and syringyl units, whereas thioacidolysis only took into account units linked by two  $\beta$ -O-4 bonds, which explains the differences in the monomer ratios. As shown in Table 2, the poplar ammonia lignin had a higher relative percentage of syringyl units than the poplar organosolv lignin. The high syringyl content of ammonia lignins has been observed previously and is attributed to mobilised syringyl lignins at particle surfaces.<sup>19</sup> The selective extraction of this syringyl rich lignin is not fully understood but could be linked to thermal properties such as glass transition temperature, which depends on the syringyl/guaiacyl ratio.

The GPC analysis of the AFEX and soda lignins from wheat straw (Fig. 2A) shows that both lignins exhibited similar  $M_w$  profiles with the exception of the higher relative abundance of the low  $M_w$  fraction eluting at 13–14 min from the soda lignin. In the case of the poplar lignins, the high-temperature organo-





**Fig. 1** HSQC NMR spectrum of Poplar ammonia lignin. Contours are colour coded according to the linkage they are assigned to. Black cross peaks correspond to currently unassigned signals. NMR spectra were recorded on a 500 MHz spectrometer at a concentration of 100 mg of the substrate in 0.6 ml of DMSO- $d_6$ .

solvent pretreatment led to partial cleavage of the alkyl-aryl ether linkages and reduced the  $M_w$  of the lignin, as shown by the higher relative intensity of the low  $M_w$  fraction eluting at 13–14 min, whereas the higher molecular weight of the ammonia lignin suggested that in the alkaline medium the lignin was solubilised without any significant cleavage of the alkyl-aryl linkages.

## 2.2. Catalytic conversion of lignin preparations

**2.2.1. Molecular weight distributions of the depolymerised products.** The four lignin preparations were subjected to catalytic conversion at 300 °C under 20 bar of  $H_2$  and their products of reactions were analysed by gel permeation chromatography. For comparison, the thioacidolyzed products of the four different lignins were also analyzed by GPC (Fig. 2C). The GPC analysis of the catalytic depolymerisation products was performed on the combined methanol-water and acetone-soluble products. This allowed the analysis of the total products, as no residual lignin insoluble in acetone was found. Moreover, the mass loss of the catalyst after thermogravimetric analysis was in the same range from each substrate and suggested that only 3% of the lignin was deposited on the catalyst (Fig. S2†). The GPC analysis gave an overview of the mass distribution but the quantification of the monomeric fraction was inaccurate due to peak width and variation of UV responses between molecules. GC analysis was therefore performed to quantify the monomers. After selective cleavage of alkyl-aryl ether bonds by thioacidolysis, it was evident that the wheat soda lignin in particular retained a high- $M_w$  (Fig. 2B) peak, eluting at 12–13 min, which presumably corresponds to the abundant condensed fraction in this lignin preparation. However, in the GPC profiles of all the other depolymerised lignins, a high- $M_w$  peak eluting at 12–13 min was present (Fig. 2C), converging towards constant relative intensity for all the four samples. It can be inferred that where there was a

large uncondensed fraction before the catalytic reaction, a substantial part of this fraction was converted to a condensed material of high  $M_w$  rather than to monomers. In the case of the initially condensed wheat soda lignin, however, there was little uncondensed material and thus there was little scope for further condensation; a slight degradation of some of the C–C linkages in the condensed fraction occurred, leading to a minor loss of relative intensity in the high- $M_w$  GPC peak (Fig. 2C).

Thus hydrogenolysis was more efficient than thioacidolysis for the depolymerisation of the highly condensed soda lignin. However, when the starting material was less condensed, *e.g.* the AFEX and ammonia lignins, hydrogenolysis was less efficient than thioacidolysis in breaking down the lignin to low molecular weight fragments.

**2.2.2. Yields and distributions of catalytically depolymerised products from the different lignins.** The analysis of the monomeric fraction of the depolymerised products was performed by GC/MS and permitted the identification of 18 monomeric aromatic structures, which are shown in Fig. 3. The major products were alkylated phenolic compounds belonging to the class described previously.<sup>6,7,10</sup> The absence of hydrogenation of the aromatic ring can be inferred from the abundance of cross peaks in the 2D NMR aromatic region (Fig. S3†) and from the absence of cyclohexanols. Deoxygenation was mainly restricted to the alkyl chain, as no hydrocinnamyl structures were produced from Poplar lignin. Moreover, except for the organosolv lignin, no significant difference in the syringyl/guaiacyl ratio was observed after catalytic depolymerisation compared to thioacidolysis (Table S1†).

As opposed to the GPC analysis, the quantification of the monomers gave significant differences. As shown in Table 3, the blank reaction without a catalyst showed the lowest overall yield of 3.5% and mainly generated guaiacol and syringol. In



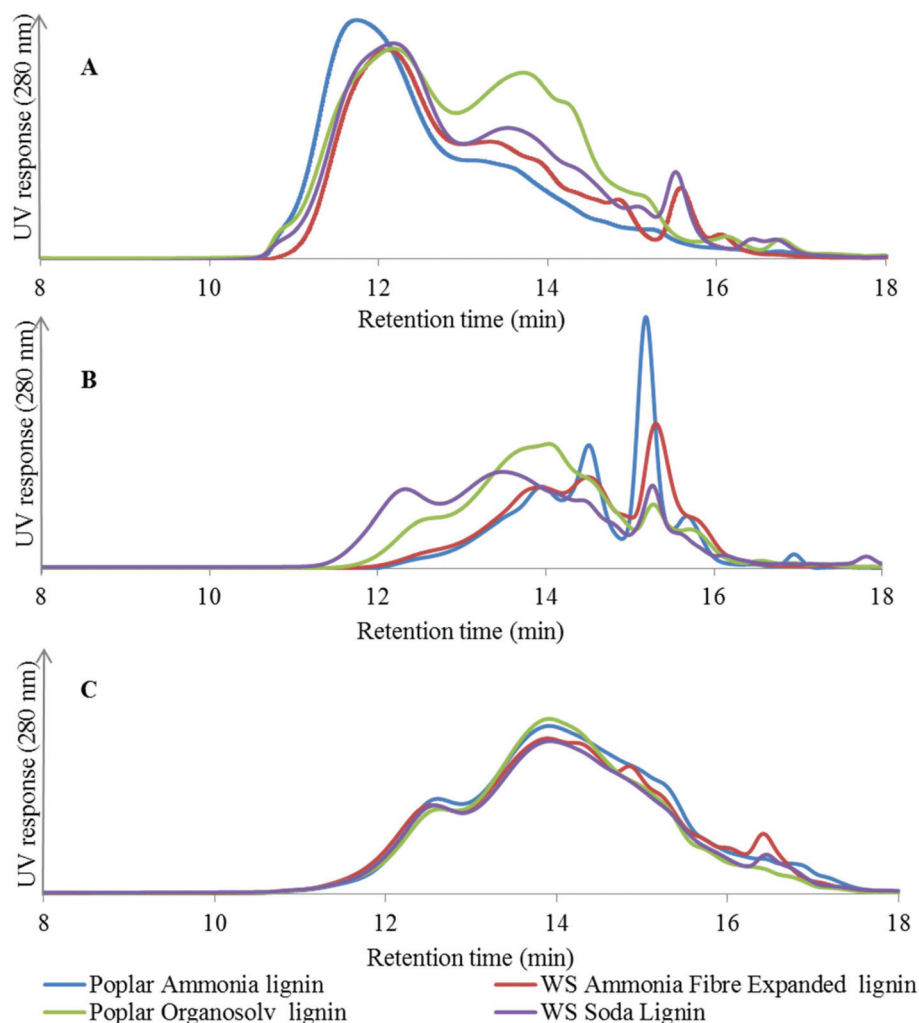


Fig. 2 GPC profiles of acetylated starting lignin (A), thioacidolysis products (B) and acetylated products of the catalytic depolymerisation at 300 °C and 20 bar H<sub>2</sub> (C).

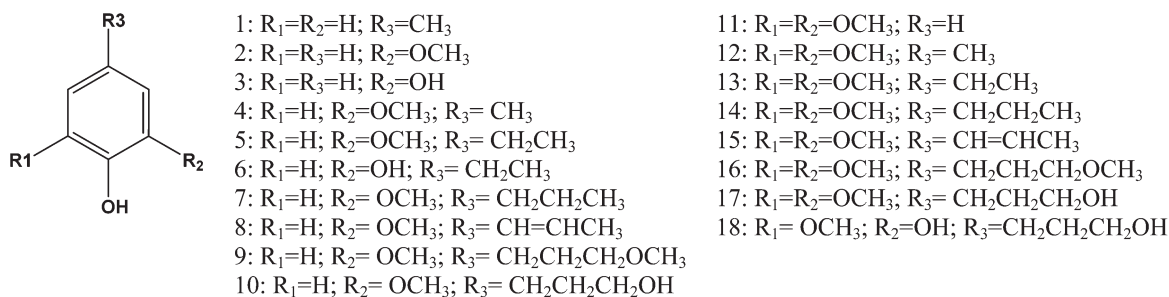


Fig. 3 Products identified after catalytic depolymerisation of different lignins.

the presence of a catalyst, the overall yield increased up to 14% for the Poplar ammonia lignin, which was nearly three times the yield obtained for the soda wheat straw lignin. In previous studies, the hydrodeoxygenation of lignins using the same type of the catalyst was conducted at lower temperatures (200 °C) which, with other influences such as the lignin structure, could explain the lower yield obtained.<sup>6</sup>

In order to compare the catalytic depolymerisation yields with the degree of condensation as measured by wet chemical analysis (thioacidolysis) both sets of data were converted to  $\mu\text{mol g}^{-1}$  of lignin monomers taking into account the molecular weight of each product.

In thioacidolysis, the selective cleavage of  $\beta$ -O-4 bonds generates products with an intact propyl side chain.<sup>21</sup> This



**Table 3** Identification and quantification of the main monomeric products from catalytic depolymerisation of different lignin preparations at 300 °C and 20 bar H<sub>2</sub>

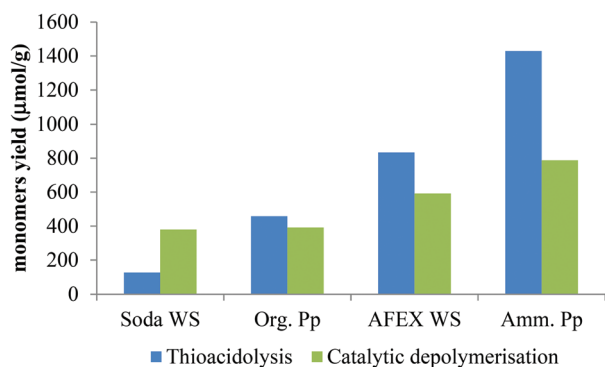
N <sup>o</sup>	Name	Ammonia poplar <sup>a</sup> (no Cat)	Ammonia poplar	Organosolv poplar	Ammonia fibre expanded WS	Soda WS
1	Methylphenol	n.d.	n.d.	n.d.	0.06	0.08
2	Guaiacol (G)	0.45 <sup>b</sup>	0.45	0.46	0.68	0.79
3	Catechol	0.12	0.13	0.12	0.19	0.21
4	MethylG	0.10	0.20	0.30	0.37	0.30
5	EthylG	0.18	0.53	0.44	2.05	1.10
6	Ethylcatechol	n.d.	n.d.	n.d.	0.11	0.07
7	PropylG	n.d.	0.85	0.56	0.84	0.19
8	PropenylG	0.15	0.85	0.28	0.63	0.08
9	3-MethoxypropaneG	n.d.	0.47	0.12	0.53	n.d.
10	3-HydroxypropaneG	n.d.	0.66	0.20	0.29	0.07
11	Syringol (S)	1.65	1.75	0.97	0.86	1.47
12	MethylS	0.21	0.56	0.46	0.23	0.29
13	EthylS	0.28	1.01	0.45	0.62	0.61
14	PropylS	0.08	2.68	1.14	0.75	0.28
15	PropenylS	0.26	1.70	0.52	0.60	0.08
16	3-MethoxypropaneS	n.d.	0.86	0.22	0.41	n.d.
17	3-HydroxypropaneS	n.d.	1.30	0.24	0.24	0.03
18		n.d.	n.d.	0.09	0.25	0.07
	Total	3.48	14.02	6.56	9.68	5.74

<sup>a</sup> Blank reaction without a catalyst. <sup>b</sup> g per 100 g of lignin.

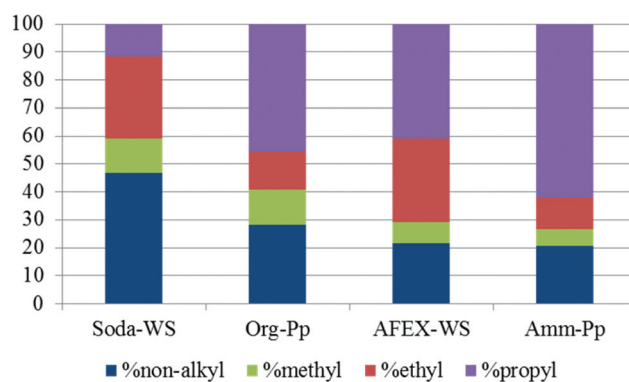
approach may be envisaged as a model reaction for the conversion of uncondensed lignin to monomeric propylphenol compounds and compared with the catalytic reaction. As shown in Fig. 4, the catalytic conversion yield was higher than the thioacidolysis yield for highly condensed lignin (soda lignin). When the uncondensed fraction of the lignin was greater, the catalytic conversion yield increased but at a lower rate than the thioacidolysis yield. The thioacidolysis yields from the soda lignin were three times lower than that from the organosolv lignin, while the catalytic yields were the same. A number of potential side-reactions in the catalytic conversion of condensed lignins are not paralleled in thioacidolysis, such as a loss of the  $\gamma$ -carbon. Moreover, abnormal constituents such as ferulic acid, coniferaldehyde and benzaldehyde units lead to monomers that are not taken into account in the thioacidolysis yields. For example, wheat lignins are rich in ferulic acid which can undergo decarboxylation, explaining the abnormal amount of ethylguaiacol (see Table 3). Moreover, small quan-

tities of guaiacol and syringol are produced even from condensed parts of the lignin structure. As shown in Fig. 5, guaiacol and syringol together accounted for 47% of the molar quantity of depolymerised products from soda lignin while they only accounted for 28%, 22% and 21% of the total molar fraction for the organosolv, AFEX and ammonia lignins, respectively. In contrast the relative proportion of propylphenolics increased from 12% to 62% of the total on going from the soda lignin to the ammonia lignin.

As the ethyl, methyl and non-alkylated phenolic compounds can come from the condensed fraction of the lignin, only the proportion of propylphenolic compounds generated can be directly correlated to the amount of  $\beta$ -O-4 linkages in the starting lignin material. As shown in Fig. 6, there is an excellent correlation between the thioacidolysis and catalytic depolymerisation yields of the products with 3-carbon side chains when either guaiacyl or syringyl units are considered.



**Fig. 4** Overall yields of monomers from thioacidolysis and catalytic conversion of different lignin preparations [blue stick: thioacidolysis products; green stick: depolymerised products].



**Fig. 5** Relative molar proportion of catalytic depolymerisation products from different lignins [blue: non-alkyl; green: methyl; red: ethyl; purple: propyl].



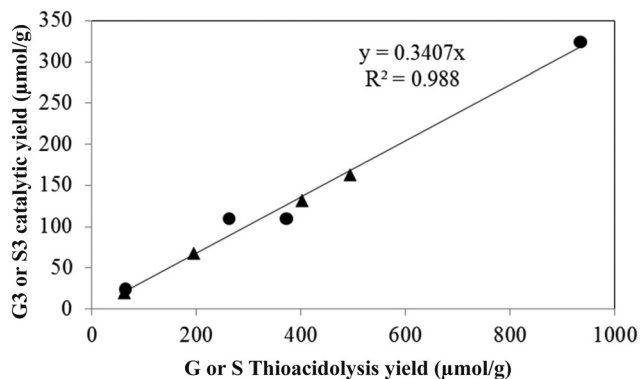


Fig. 6 Correlation between thioacidolysis and catalytic depolymerisation yields of the propylphenolic products (circle: sum of S3 type catalytic products; triangle: sum of G3 type catalytic products).

This observation suggests that both guaiacyl and syringyl units undergo the same type of complex reactions at the same rate. The catalytic depolymerisation yield of propylphenolic compounds was three times lower than its potential maximum yield as deduced from thioacidolysis.

### 3. Discussion

The results presented above show that the structure of the lignin greatly affects the nature and yield of monomeric depolymerised products. Consequently, the cost efficiency of the lignin isolation method – usually dominated by the efficiency of conversion of the associated cellulose to biofuel – must be balanced against the potential to generate products of higher added values.

Compared to the analytical technique of thioacidolysis, the catalytic conversion was non-selective towards uncondensed linkages, giving rise to both cleavage and condensation. In consequence, the catalytic conversion was less efficient for depolymerising uncondensed lignins. In other words catalytic conversion of lignin to fine chemicals is the most promising when the starting lignin is uncondensed, but condensation of the lignin during the catalytic step then leads to the greatest unfulfilled potential. Lignin condensation during this step is as much an issue as during the isolation of the lignin. As shown in Fig. 7, competition between depolymerisation and condensation is the key problem in the conversion of lignin into fine chemicals.

This competition exists at all stages of the process, from feedstock pretreatment to catalytic depolymerisation. The ammonia percolation pretreatment, in which the lignin was continuously removed from the reaction vessel as soon as it

became soluble, avoided condensation by limiting both depolymerisation and the simultaneous generation of unstable intermediates.<sup>15</sup> During catalytic conversion, depolymerisation is the aim and the generation of unstable products cannot be avoided. The key effect of the hydrogenolysis was to reduce condensation of the products by fast stabilisation (hydrogenation) of reactive intermediates. However, the results showed that condensation still predominated during the catalytic reaction.

Further optimisation of the catalytic conversion of lignin to fine chemicals requires the condensation process to be prevented. For a decade it has been known that one of the condensation pathways is a nucleophilic attack on the benzylic position of the lignin structure (Fig. 8).<sup>22,23</sup> This type of reaction predominates in acid catalysed organosolv reactions. During catalytic conversion, the slightly acidic alumina support may promote the acid-catalysed alkylation of the benzylic position, as has been previously reported for the condensation of benzylphenyl ether on zeolite HSZM-5 in aqueous medium.<sup>24</sup>

In the case of bio-oil deoxygenation, a two-temperature process has been suggested with the aim of stabilizing the reactive species and thus avoiding condensation.<sup>25</sup> A similar approach to stabilisation of lignin before hydrogenolysis will be considered in a future paper. Another explanation for the low conversion of lignin can be inferred from the blank reaction where no catalyst was added to the medium. GPC analysis of the ammonia lignin subjected to these conditions showed a similar molecular weight distribution to the catalytic products (data not shown), implying that condensation could also occur in solution. In that case, slow adsorption of lignin fragments on the catalyst could also be the limiting factor for lignin conversion. A similar observation motivated other authors to

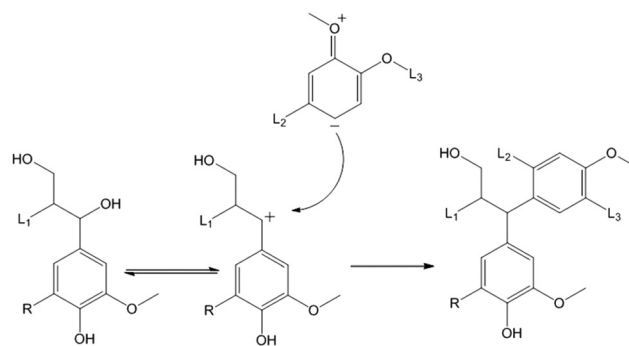


Fig. 8 Condensation of the lignin *via* benzylic carbonium ion formation after heterolytic cleavage of the benzylic C–O bonds [ $L_1$ ,  $L_2$ ,  $L_3$  = lignin fragments;  $R$  = H or OMe].

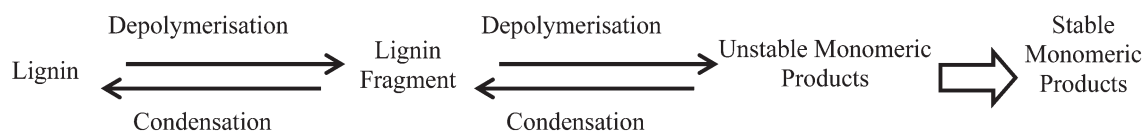


Fig. 7 Lignin depolymerisation/condensation scheme.



subject lignin to liquid phase reforming (LPR) followed by HDO.<sup>26</sup> While the lignin products changed, the two step process did not improve the overall yield compared to LPR alone. In other words, LPR treated lignin, probably more condensed, was also less suitable for HDO conversion.

It can be expected that conversion of highly uncondensed lignins, such as AFEX or ammonia lignin, will require gentle and carefully optimised conditions to achieve selective cleavage of C–O bonds and generate high yields of fine aromatic chemicals. In the case of more condensed lignins such as soda or organosolv lignins, harsher conditions are required to cleave C–C bonds or other cracking approaches should be envisaged.

## 4. Conclusion

The lignin structure, in particular the abundance of  $\beta$ -O-4 linkages, had a major impact on the yield and distribution of products after catalytic depolymerisation. Increasing the degree of condensation in the initial lignin structure reduced the total yield of monomers and also reduced the proportion of monomers retaining the three-carbon alkyl side-chain, which have particular potential for conversion to fine chemicals. When the initial lignin structure was relatively uncondensed, condensation during the catalytic step reduced the yields of alkylated monomers. Optimisation of lignin breakdown, especially from highly uncondensed lignin, requires more selective cleavage methods to minimise condensation. It may be advantageous to adopt a multi-stage breakdown strategy with increasing severity of conditions at each stage.

## 5. Experimental

### 5.1. Materials

Hybrid poplar sawdust was provided by a UK sawmill. The sawdust was sieved and particles of size ranging from 125  $\mu\text{m}$  to 1080  $\mu\text{m}$  were used. The dry matter content of the poplar sawdust was 92.6%. Ammonia fibre expanded (AFEX) wheat straw was obtained from Prof. Bruce Dale, Michigan State University. Protobind 1000 lignin (soda lignin) was purchased from Green Value (Switzerland).

The alumina supported platinum catalyst was obtained from Johnson Matthey (reference number 1074). The catalyst was sieved between 250 and 425  $\mu\text{m}$ , pre-reduced at 250  $^{\circ}\text{C}$  and stored under air. The platinum dispersion, as measured by carbon monoxide chemisorption, was 56%, while the catalyst had a BET surface area of 119  $\text{m}^2 \text{g}^{-1}$ , a pore volume of 0.49  $\text{cm}^3 \text{g}^{-1}$  and an average pore diameter of 11 nm. All other reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

### 5.2. Lignin preparation

Three of the four tested lignins were prepared in house, as described below.

**5.2.1. Lignin isolation from AFEX wheat straw.** Following Lawther *et al.*,<sup>27</sup> the AFEX wheat straw was extracted under

reflux at 5% loading with 0.5 N sodium hydroxide in ethanol–water (6/4; v/v). After this mild extraction step, the mixture was filtered on a Buchner funnel and the residue washed with ethanol–water (6/4). After neutralisation of the filtrate to pH 6, hemicelluloses were precipitated by adding 3 volumes of ethanol. The precipitate was removed by centrifugation and the supernatant was concentrated and acidified to pH 2. The precipitated lignin (AFEX WS) was recovered by centrifugation, washed with deionised water and freeze dried.

**5.2.2. Acid organosolv lignin from poplar.** This lignin was prepared by a well-established organosolv process<sup>28</sup> as previously described.<sup>29</sup> In a stainless steel reactor, poplar sawdust was mixed with ethanol–water (6/4, v/v) containing sulphuric acid (1.25% w/w of poplar). The reactor was rotated on a motor-driven shaft inside a programmable oven. The reaction was conducted at 180  $^{\circ}\text{C}$  for 1 h. After cooling, the mixture was filtered on a Buchner funnel and the filtrate was diluted in 3 volumes of water (pH 2). The precipitated lignin (Organosolv Poplar) was recovered after centrifugation, washed with deionised water and freeze dried.

**5.2.3. Ammonia lignin from poplar.** Ammonia lignin was prepared as reported previously.<sup>15</sup> Briefly, aqueous ammonia (15% w/v) was percolated through the poplar sawdust at 180  $^{\circ}\text{C}$ , 20 bar and 3  $\text{ml min}^{-1}$  flow rate with a total liquid/solid ratio of 10:1. The percolated liquor was concentrated and acidified to pH 2. The precipitate was recovered by centrifugation and briefly hydrolysed with mild ethanolic acid to remove carbohydrate impurities. The lignin was then precipitated in three volumes of water (pH 2, HCl). The purified lignin was recovered by centrifugation, washed three times with deionised water and freeze dried.

### 5.3. Catalytic conversion of the lignin

The catalytic depolymerisation reactions were conducted in a 300 ml 316 stainless steel Parr batch autoclave reactor equipped with a Parr model 4842 digital temperature controller  $\pm 2$   $^{\circ}\text{C}$ . During a typical experiment 0.5 g of lignin was added to the autoclave along with 0.1 g 1% w/w Pt/ $\text{Al}_2\text{O}_3$  and 100 ml methanol–water mix (50:50 v/v). The reactor was purged with hydrogen and pressurised to 20 bar. The reaction was performed at 300  $^{\circ}\text{C}$  with mechanical stirring (1000 rpm) and stopped after 2 h (plus 30 min ramp time). The reaction mixture was filtered on a sintered glass (porosity 3) to remove the catalyst and insoluble products, and then the residue was washed with acetone to solubilise higher molecular weight lignin fragments. The fraction soluble in methanol–water was centrifuged to remove finely dispersed solids. An aliquot of the solution was then mixed with a known quantity of an internal standard, acidified to pH 3 and extracted with dichloromethane–dioxane (8/2 v/v). After evaporation of the solvent, the products were solubilised in 2 ml dichloromethane.

### 5.4. Analytical methods

Sugar analysis, gel permeation chromatography and thioacidolysis of lignins have been described in a previous paper.<sup>15</sup> For GPC analysis of the catalytic conversion products, equal



volumes of the methanol–water and acetone solubles were mixed together, evaporated to dryness, acetylated, and solubilised in THF before injection. GC/MS analysis of the catalytic conversion products was performed as follows. An aliquot (10  $\mu$ l) of the products, extracted in dichloromethane, was added to 30  $\mu$ l pyridine and 70  $\mu$ l TMS. Qualitative and quantitative analyses were performed using a Shimadzu GC-MS-QP2010S coupled to a Shimadzu GC-2010 GC equipped with a ZB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). The quantification of the products was measured on the TIC and based on reference compounds with hexadecane as an internal standard.

NMR spectra were acquired on a Bruker Avance III 500 MHz spectrometer equipped with a BBFO + probe. The central DMSO solvent peak was used as the internal reference ( $\delta_C$  39.5,  $\delta_H$  2.49 ppm). The  $^1H$ ,  $^{13}C$ -HSQC experiment was acquired using the standard Bruker pulse sequence 'hsqcetgppsp.3' (phase-sensitive gradient-edited-2D HSQC using adiabatic pulses for inversion and refocusing). The composite pulse sequence 'garp4' was used for broadband decoupling during acquisition. 2048 Data points were acquired over 12 ppm spectral width (acquisition time 170 ms) in the F2 dimension using 24 scans with 1 s interscan delay and the d4 delay was set to 1.8 ms ( $1/4J$ ,  $J = 140$  Hz). Spectral width of 170 ppm, 256 increments were acquired in F1 dimension (acquisition time 5.6 ms) resulting in a total experimental time of 2 h. The spectrum was processed using squared cosine bell in both dimensions and LPfc linear prediction (32 coefficients) in F1. Volume integration of cross peaks in the HSQC spectra was carried out using MestReNova software.<sup>17</sup>

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